



PCT/AU00/00631 #2

AU001631

REC'D 27 JUN 2000

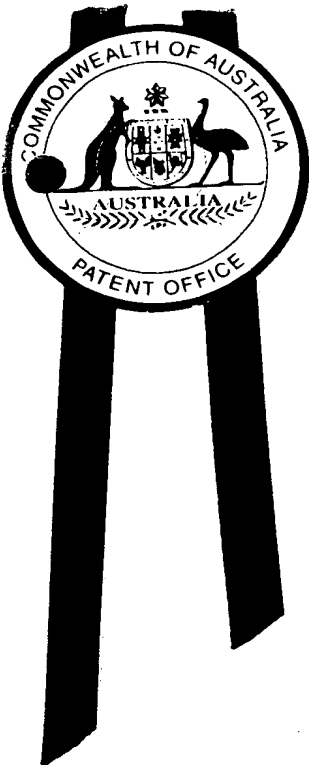
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I, KAY WARD, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PQ 0788 for a patent by CERAMIC FUEL CELLS LIMITED filed on 04 June 1999.



WITNESS my hand this  
Twenty-second day of June 2000

*K Ward*

KAY WARD  
TEAM LEADER EXAMINATION  
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**CERAMIC FUEL CELLS LIMITED**

**A U S T R A L I A**

**Patents Act 1990**

**PROVISIONAL SPECIFICATION**

for the invention entitled:

**"A FUEL CELL GAS SEPARATOR"**

The invention is described in the following statement:

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## A FUEL CELL GAS SEPARATOR

The present invention relates to solid oxide fuel cells and is particularly concerned with gas separators between adjacent fuel cells.

5

The purpose of a gas separator in planar fuel cell assemblies is to keep the oxygen containing gas supplied to the cathode side of one fuel cell away from the fuel gas supplied to the anode side of an adjacent fuel cell and to conduct heat generated in the fuel cells away from the fuel cells. The gas separator may also conduct electricity generated in the fuel cells  
10 away from the fuel cells, but this function may alternatively be performed by a separate member between each fuel cell and the gas separator.

Sophisticated ceramics for use in fuel cell gas separators have been developed which are electrically conductive, but these suffer from a relatively high fragility, low thermal  
15 conductivity and particularly high cost. Special alloys have also been developed, but it has proved difficult to avoid the various materials of the fuel cell assembly and the interfaces between them degrading or changing substantially through the life of the fuel cell, particularly insofar as their electrical conductivity is concerned, because of the tendency of different materials to interact at the high temperatures which are required for efficient operation of a  
20 solid oxide fuel cell. For example, most metallic interconnects contain substantial quantities of the element chromium which is used to impart oxidation resistance to the metal as well as other properties.

It has been found that where chromium is present in more than minute quantities it may  
25 combine with oxygen or oxygen plus moisture to form highly volatile oxide or oxyhydroxide gases under conditions which are typical of those experienced in operating solid oxide fuel cells. These volatile gases are attracted to the cathode-electrolyte interface where they may react to form compounds which are deleterious to the efficiency of the fuel cell. If these chromium reactions are not eliminated or substantially inhibited, the performance of the fuel  
30 cell deteriorates with time to the point where the fuel cell is no longer effective. Several of

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these alloys and one proposal for alleviating this problem are described in our patent application WO96/28855 in which a chromium-containing gas separator is provided with an oxide surface layer which reacts with the chromium to form a spinel layer between the substrate and the oxide surface layer and thereby tie in the chromium. However, these  
5 specialist alloys remain too expensive for substantial use in fuel cell assemblies.

Special stainless steel have also been developed which are stable at high temperature in the atmospheres concerned, but they generally contain substantial amounts of chromium to provide the desired oxidation resistance, leading to the problems described above so that  
10 special coatings or treatments are required to prevent the chromium-based gases escaping from the gas separator. Another approach to a heat resistant steel gas separator is described in our patent application PCT/AU98/00956. However, once again, all of these heat resistant steels are specialist materials whose cost will remain high unless substantial amounts can be produced. Furthermore, the thermal and electrical conductivity of heat resistant steels is low  
15 relative to many other metals and alloys, for example, 22 - 24 W/m.K compared to 40-50 W/m.K for the Siemens-Plansee alloy described in WO96/28855. To compensate for this, the thickness of the steel gas separator has to be increased, increasing the mass and cost of a fuel cell stack.

20 We have now surprisingly found that copper-based gas separators may be successfully utilised in solid oxide fuel cell assemblies without poisoning the anode and the present invention may accordingly provide, in a first aspect, a gas separator member for a planar fuel cell comprising a layer of solid oxide electrolyte, an anode layer and a cathode layer, the gas separator member having an anode side and a cathode side and comprising a layer of copper  
25 or copper-based alloy having a layer of oxidation-resistant material on the cathode side.

Copper is approximately fourteen times a better thermal conductor than typical heat resistant steels so that considerably less copper may be required to provide the desired heat transfer rate. For example, a heat resistant steel gas separator requiring a 4 mm thickness to  
30 achieve the required heat transfer rate may be replaced by a gas separator in accordance with

the invention having a copper layer thickness of about 0.3 mm. This combined with the substantially reduced cost of copper over the specialist heat resistant steels can greatly reduce the cost and mass of a solid oxide fuel cell stack.

5       The layer of copper preferably has a thickness in the range 0.25 mm to 1 mm, more preferably 0.4 mm to 0.7 mm. At thicknesses less than 0.3 mm, it is unlikely that the copper layer will have sufficient bulk to provide the desired thermal transfer at normal solid oxide fuel cell power densities. However, at lower power densities, thinner copper layers may be adequate, for example 0.1 mm or less. Thicknesses greater than about 0.7 mm are  
10 unnecessary for pure copper. However, the copper may be alloyed with other elements up to a maximum of 50 wt%, preferably up to 20 wt%, in which case a thickness greater than 1 mm, for example up to 4 mm, may be required to provide the desired thermal transfer. Possible alloying elements include Al, Ni, Zn, Sn, Fe, Be, Ag, Au, Mn, Si, P, and Pb singly or in combinations of two or more.

15

A major advantage of alloying the copper in the copper layer with aluminium is that it may form the layer of oxidation-resistant material on the cathode side automatically on being exposed to an oxygen containing gas at elevated temperature, for example in use of the fuel cell gas separator, and there is accordingly provided in a second aspect of the invention  
20 a gas separator member for a planar fuel cell comprising a layer of solid oxide electrolyte, an anode layer and a cathode layer, the gas separator member being formed of aluminium bronze.

Aluminium bronze comprises copper with at least 4 wt%, more usually at least 5 wt%  
25 Al. The ability of the aluminium bronze to form an oxidation resistant layer of  $\text{Al}_2\text{O}_3$ , and therefore the oxidation resistance of the gas separator member, is very much greater at 5 wt% Al than at 4 wt% Al, but does not increase greatly with further increases in aluminium content. Aluminium bronzes have been made with 14 wt% Al or more, but generally they will have no more than 10 wt% Al. The inclusion of processing aids and other additives such  
30 as Fe, Sn and other elements in aluminium bronzes is well known.

The aluminium bronze may be pretreated by heating to at least 650°C, possibly at least 750°C, in air or other oxygen containing gas to form the  $Al_2O_3$  layer on the cathode side of the gas separator, but preferably, as noted above, the oxidation resistant layer is formed in use of the gas separator member.

5

Aluminium bronze is considerably less thermally conductive than pure copper, so that greater thicknesses than 0.7 mm may be required, for example up to 2 mm to provide the desired heat transfer at normal power densities.

10 Alternatively, the layer of oxidation resistant material on the cathode side of the gas separator may be applied to the layer of copper or copper-based alloy, or vice versa. Since the layer of oxidation-resistant material is primarily preventing access of the oxygen containing gas on the cathode side of the fuel cell to the copper or copper-based alloy layer, it need not be a thick layer, for example, in the range 50 to 1000 microns, preferably up to 15 200 microns, more preferably up to 100 microns, depending upon the type of layer. The layer of oxidation-resistant material may take any of a variety of forms, such as foils which are wrapped around the copper or copper-based alloy, or otherwise attached to it to prevent access of the oxygen containing gas, coatings, or substrates onto which the copper or copper-based alloy layer is coated. The copper or copper-based alloy could be coated onto a 20 substrate layer of oxidation resistant material by sputtering or any other suitable coating technique. The preferred foil or substrate material is heat resistant steel, which may itself be coated with alumina on the cathode side or be a self-aluminizing heat resistant steel to prevent chromium gas escaping and poisoning the cathode in use of the gas separator.

25 Where the copper or copper-based alloy layer is coated with the oxidation-resistant material, this may be by vapour deposition or any of a variety of known processes. The oxidation resistant layer may itself comprise multiple layers to provide the desired properties.

30

In a further embodiment, the oxidation resistant material may comprise  $\text{Al}_2\text{O}_3$  applied to the layer of copper or copper-based alloy as an alumina coating or as an aluminium coating which is subsequently oxidised. Aluminium may be applied to the copper or alloy surface by a suitable metal spraying technique such as combustion metallising, low or high velocity oxy-fuel processes, electric arc processes, plasma flame processes, or by other vapour deposition processes or even by plating. The aluminium coating may then be oxidised to provide the alumina layer, but preferably the aluminium is first permitted to diffuse into the copper or alloy surface layer by reacting it at elevated temperature, preferably above the melting temperature of the aluminium, in a controlled atmosphere of an inert gas, a reducing atmosphere or possibly even an oxidising atmosphere. Diffusion is preferably continued until there is no continuous Al layer on the copper or alloy surface, but with at least 5 wt% Al at the exposed surface which is then oxidised to form a continuous alumina layer.

Copper has a sufficient vapour pressure at the operating temperature of at least  $750^\circ\text{C}$  of a solid oxide fuel cell that copper vapour may contaminate the active surface of the anode layer of the fuel cell. Where the fuel gas is hydrogen, this has proven not to be a major disadvantage so that the copper may remain exposed to the anode layer of the fuel cell. However, the anode layer is commonly of a nickel material and it has been proposed to use the nickel in the anode as a catalyst for reforming methane in the fuel gas to hydrogen. The copper vapour has been found to interfere strongly with this catalytic efficiency of the nickel. Thus, where the fuel gas includes methane and the anode layer includes nickel, it may be necessary to provide a protective layer also on the anode side of the layer of copper or copper-based alloy. Such a protective layer has not been found to be necessary when the copper-based alloy layer is an aluminium bronze as described above since it appears the Cu vapour is prevented from escaping by the alumina layer.

The protective layer on the anode side may comprise heat resistant steel or alumina as described above and, for example, the copper or copper-based alloy layer may be wrapped entirely in the heat resistant steel foil so that only the thermal conductivity properties of the copper or alloy are being used. Again, a heat resistant steel protective layer on the anode side

may have a thickness as described above, preferably in the range 50-100  $\mu\text{m}$ . An  $\text{Al}_2\text{O}_3$  protective layer may have a thickness as small as 1 - 3  $\mu\text{m}$ , but greater thicknesses as described above may be acceptable.

- 5 Alternatively, the protective layer on the anode side may comprise multiple layers. In one embodiment a metal barrier layer of any one of W, Ta, or Nb or alloys of one or more of these metals which do not dissolve into the copper may be provided on the copper or copper-based alloy layer, followed by an intermediate layer of Ag plus an outer barrier layer of Ni, a noble metal except Ag or an alloy of one or more of these metals. The metal barrier layer
- 10 acts to prevent the Cu vapour escaping to poison the Ni-containing anode. However, W, Ta and Nb may oxidize to their oxides at the relatively high operating temperatures of a solid oxide fuel cell even in the relatively low oxygen partial pressures on the fuel side of the fuel cell and/or react with hydrocarbons or  $\text{CO}_2$  to form carbides, and the Ag layer is provided to alleviate this. The metal or metals of the metal barrier layer and of the outer barrier layer
- 15 do not react with Ag, but they may react with each other and the Ag is also provided to alleviate this. Ag acts as a catalyst to convert methane to ethane which is not desired, so Ag is not an acceptable outer barrier layer metal. The outer barrier layer is provided to prevent this. Similar protective layers on a Cr-based gas separator are described in our patent application WO97/35349, the contents of which, including any corresponding US patent
- 20 granted on US Patent Application 09/155061, are incorporated herein by reference.

Each layer of a multiple layer protective layer preferably has a thickness in the range of 2 - 3  $\mu\text{m}$ . However, layers in the range of 1 - 30  $\mu\text{m}$  may be acceptable. Greater thicknesses than 30  $\mu\text{m}$  may lead to one or more of the multiple layers of the protective layer

25 separating in use due to the different coefficients of thermal expansion of the metals.

The gas separator in accordance with the present invention may have gas channels formed on opposed sides, for example as described in our aforementioned patent applications WO96/28855 and WO97/35349. However, preferably, the gas flow passages are formed in

30 or provided by a mesh or other structure provided between the respective side of the gas



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separator and the adjacent electrode, for example as described in our patent application WO98/57384.

The gas separator may provide a path for drawing electricity from the fuel cell given  
5 the high electrical conductivity of copper, but it may be desirable to utilize a separate electrical conductor between the gas separator and the respective electrode particularly when the layer of oxidation-resistant material and/or any protective layer is formed of an electrically insulating material such as alumina. One proposal for a separate silver electrical conductor on the cathode side and separate nickel electrical conductor on the anode side is  
10 disclosed in our patent application WO99/13522.

The possibility of using copper as a material for a gas separator in a solid oxide fuel cell assembly was tested over an extended period by verifying whether any poisoning of a nickel anode by the copper resulted in substantially reduced performance of the fuel cell  
15 assembly. The results, given by way of example only, are shown in Figure 1 which is a graph showing cell voltage output over about 1,030 hours.

In the example, a stack of four fuel cell assemblies was formed with each fuel cell assembly being substantially as described with reference to Figure 4 in our aforementioned  
20 patent application WO 99/13522, except that two of the nickel meshes on the anode sides of the fuel cells were replaced by copper meshes and the silver meshes were replaced by platinum mesh. However, silver mesh could have been used in place of the platinum mesh. Each of the meshes may be, for example, woven, punched sheets or expanded sheets. Thus, each fuel cell comprised a solid oxide electrolyte of  $Y_2O_3$  - doped  $ZrO_2$  as an ionic conductor,  
25 an anode comprising an  $Ni/ZrO_2$  cement and a cathode comprising strontium doped lanthanum manganite (LSM). Each gas separator between adjacent fuel cells and adjacent the two end fuel cells was formed of self-aluminising heat resistant steel with gas channels formed on the side or sides facing the adjacent fuel cell or cells. A platinum mesh with platinum connectors was disposed between the cathode of each fuel cell and the adjacent gas separator, while a  
30 nickel mesh was disposed between the anodes of two of the fuel cells and the adjacent gas

separators with a copper mesh between the anodes of the other two fuel cells and the adjacent gas separators, with all of the meshes in electrical contact with the adjacent electrodes.

In the example, the fuel cells, gas separators and meshes were each 50 mm x 50 mm, with the copper mesh being woven and the nickel and platinum meshes being expanded metal. All of the stainless steel gas separators had alumina coatings on both the anode side and the cathode side. Current take-offs were of platinum wire threaded through holes in the gas separators as described in WO 99/13522 or welded to the terminal gas separators or end plates under the seal area. The fuel cell assembly was manifolded to prevent fuel gas and oxygen containing gas leakage and was tested at 900°C, at a current of three amps, with a fuel gas of humidified hydrogen containing 9.5% H<sub>2</sub>O and air as the oxygen containing gas.

In the example, the voltage was measured across each pair of cells, that is the two cells with the copper anode side current collectors and the two cells with the nickel anode side current collectors. During the test, fuel utilisation (U<sub>f</sub>) was tested, that is how much of the fuel gas inputted to the fuel cell stack was used to make electricity, by diluting with nitrogen in order to keep all flow rates and other parameters the same. Nine phases can be identified from the figure during the operating of the stack as follows:

20 Start-up Phase to 4.5 hrs

Phase I: 4.5 hrs to 25 hrs. Continuous operation at 5.5% fuel utilisation.

Phase II: 25 hrs to 260 hrs. Continuous operation at 5.7% fuel utilisation.

Phase III: 260 hrs to 285 hrs. Attempt at higher fuel utilisation through increased moisture.

25 Phase IV: 285 hrs to 455 hrs. Nitrogen dilution with fuel utilisation at 33%.

Phase V: 458 hrs to 459 hrs. Nitrogen dilution with fuel utilisation at 57 and 48%.

Phase VI: 458.8 hrs to 477.7. Nitrogen dilution with fuel utilisation at 38.6%.

Phase VII: 477.8 hrs to 963 hrs. Condition as Phase II. Continuous operation at 5.7% utilisation.

30 Phase VIII: 962 hrs to 1009 hrs. Condition as Phase II. Thermal cycle experiment.

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Phase IX: 1010 hrs to 1031 hrs. Condition as Phase II. Mechanical load removal.  
Shut-down phase.

The graph shows substantial stability of the voltage output over about 1000 hrs with  
5 very little difference between the voltages at the copper and nickel anode side current  
collectors. This shows that copper, with an oxidation resistant coating on the cathode side,  
may be used as a gas separator in a fuel cell stack given the advantageous thermal  
conductivity properties of the metal. Where hydrogen is the fuel gas, no other treatment or  
protective coating of the copper is required. However, if methane is the fuel gas and nickel  
10 the anode material, a protective coating will be required on the anode side of the copper gas  
separator. Alternatively, some other means will be required to prevent copper vapour  
escaping from the gas separator, such as alloying with aluminium. Other alloying metals, such  
as Be, may also provide the same advantage. However, Al is preferred over Be on a cost  
basis and because the oxide of Be is highly toxic.

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A variety of protective coatings on copper or copper alloy sheets have also been tested  
to determine whether the coatings prevent copper vapour contaminating the nickel in a nickel  
zirconia cermet such as is used in fuel cell anodes.

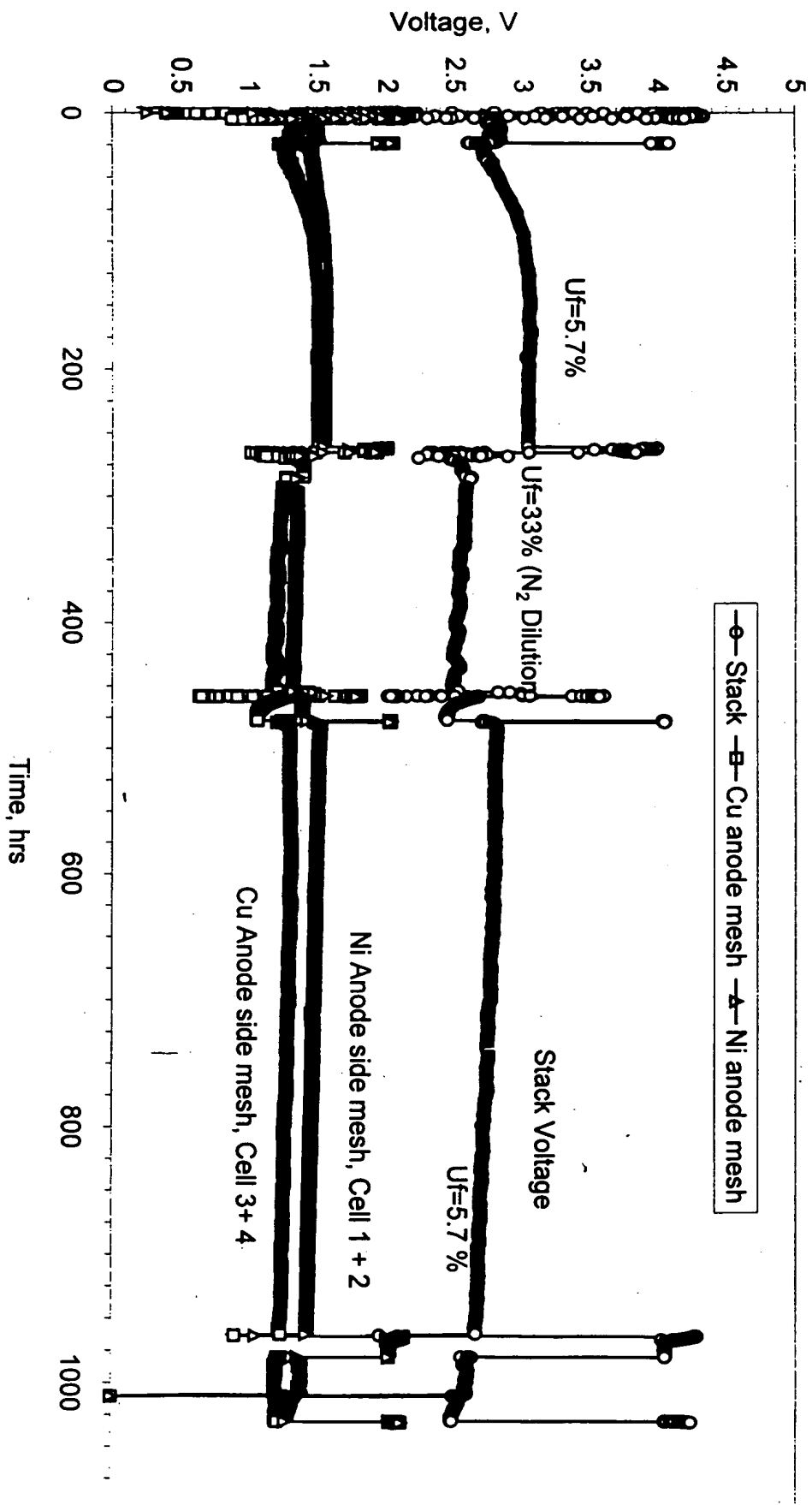
20 In a first test, a protective layer comprising three layers of, respectively, tungsten  
followed by silver and then nickel were applied to a pure copper sheet. In a second test, a  
protective layer comprising three layers respectively tantalum followed by silver and then  
nickel was applied to a similar pure copper sheet. Each of the three layers in each test had a  
thickness of 2 to 3 microns. In a third test, a similar pure copper sheet was wrapped in a self-  
25 aluminising heat resistant steel foil having a thickness of 50 microns. In a fourth test an  
aluminium bronze sheet was provided with an alumina surface coating by oxidising the sheet  
in air at 850°C for two hours.

30

Each of these protected sheets was then placed face down on a nickel zirconia cermet substrate and weighted to ensure close physical contact between the protective layer of the copper or copper alloy sheet and the anode material. The structure was then heated at 900°C for one week in purge gas (4% H<sub>2</sub> in nitrogen). At the end of the test, each structure was  
5 cooled and the nickel zirconia cermet substrates were investigated for copper contamination of the nickel. No such contamination was identified.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be  
10 understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps, features, compositions and  
15 compounds.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.  
20



FIGURE



## TENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTICE INFORMING THE APPLICANT OF THE  
COMMUNICATION OF THE INTERNATIONAL  
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:

HUNTSMAN, Peter, Harold  
Davies Collison Cave  
1 Little Collins Street  
Melbourne, Victoria 3000  
AUSTRALIE

WEDNESDAY, 27 DEC 2000

Date of mailing (day/month/year) 14 December 2000 (14.12.00)		IMPORTANT NOTICE	
Applicant's or agent's file reference 2297196/PHH			
International application No. PCT/AU00/00631	International filing date (day/month/year) 02 June 2000 (02.06.00)	Priority date (day/month/year) 04 June 1999 (04.06.99)	
Applicant CERAMIC FUEL CELLS LIMITED et al			

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:

AG,AU,DZ,KP,KR,MZ,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CR,CU,CZ,DE,DK,DM,EA,EE,EP,ES,FI,GB,GD,  
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The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 14 December 2000 (14.12.00) under No. WO 00/76015

**REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)**

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

**REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))**

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Genève 20, Switzerland	Authorized officer  J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

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